Biodiesel Technical Information

In 1912, Rudolph Diesel had been using peanut oil to operate his new engines. During a demonstration at the World's Fair, he said, "The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time." His words have taken on added significance today.

This manual is a compilation of the experiences of ADM, the biodiesel and petroleum industries, and large-scale users such as the automotive industry, regarding the technical aspects of biodiesel. Its purpose is to serve as a reference manual and to provide interested parties with basic information on biodiesel.

Should you have any questions regarding biodiesel or biodiesel blends, please feel free to contact ADM Biodiesel Technical Services at (217) 451-3608 or Biodiesel Sales at (217) 451-2566. You may also send your inquiries to biodieselsalesonline@admworld.com.

Biodiesel as a Fuel and as a Blending Component

As a Fuel

Biodiesel (B100) is defined as "a fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats." In addition, it must meet all of the parameters as defined within the ASTM specification D6751, "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels." Biodiesel has been registered with the U.S. EPA as a fuel and a fuel additive under Section 211(b) of the Clean Air Act. Biodiesel is a fuel designed as a blendstock for use in blending with petroleum diesel fuel. It is not intended for use with gasoline. Biodiesel has been proven to reduce the emissions of hydrocarbons, carbon monoxide and particulates when used alone or with blends that include petroleum diesel. Biodiesel has excellent lubricity properties and is typically low in sulfur content, thus meeting the needs of the EPA and new generation fuels.

As a Fuel Additive

Nearly every Original Equipment Manufacturer (OEM) approves the use of up to 5% biodiesel (B5) when blended with diesel fuel that meets its appropriate specifications as found within ASTM D975. In most cases, the industry believes that blends up up to 20% (B20) will cause no detriment to performance. With more than 50 million miles logged, B20 has proven to be a practical fuel that can be used in any diesel engine with few precautions or changes. However, most U.S. auto, engine and fuel injection equipment companies strongly discourage the use of blends over 20%, mainly due to the possible impacts of higher blends on equipment and fuel systems that have not been thoroughly tested. There are additional concerns regarding the influence of the increased biodiesel content greater than 20% on cold flow properties, material compatibility, maintenance intervals, fuel stability, biological growth, energy content, emissions and overall handling.

Production of Biodiesel

Production

Biodiesel is typically produced by the reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-alkyl esters (biodiesel) and glycerin. This reaction is called transesterification. Raw or refined vegetable oil or recycled greases that have not been processed into biodiesel are not biodiesel. Care must be taken to then separate the finished biodiesel from the glycerin, catalysts, soaps and any excess alcohol that may remain.

Testing

The finished B100 must be tested to comply with the ASTM D6751 requirements. These specifications are not dependent upon the oil or fat used to produce the biodiesel, or the specific process employed. However, it is critical to understand that the results, and some performance criteria, may vary based upon the feedstock used.

The conformance of the product to the ASTM specifications is a requirement for any and all tax incentives and credits. Due to the handling of hazardous materials and large quantities of flammable chemicals during the reaction, the production of biodiesel should only be undertaken by trained professionals. Federal, state and local laws may exist that require special permits for the production and handling of fatty acid methyl esters and the components used to manufacture such.

ASTM D6751-07a

STANDARD SPECIFICATION FOR BIODIESEL FUEL BLEND STOCK (B100) FOR MIDDLE DISTILLATE FUELS

PROPERTY	TEST METHOD	GRADE S15 LIMITS	GRADE S500 LIMITS	UNITS
Calcium and magnesium, combined	EN 14538	5 max	5 max	ppm (µg/g)
Flash point (closed cup)	D93	93 min	93 min	°C
Alcohol control				
One of the following must be met:				
1. Methanol content	EN 14110	0.2 max	0.2 max	% volume
2. Flash point	D93	130 min	130 min	°C
Water and sediment	D 2709	0.050 max	0.050 max	% volume
Kinematic viscosity, 40° C	D 445	1.9-6.0	1.9–6.0	mm2/s
Sulfated ash	D 874	0.020 max	0.020 max	% mass
Sulfur	D 5453	0.0015 max (15)	0.05 max (500)	% mass (ppm)
Copper strip corrosion	D 130	No. 3 max	No. 3 max	
Cetane number	D 613	47 min	47 min	
Cloud point	D 2500	Report	Report	°C
Carbon residue	D 4530	0.050 max	0.050 max	% mass
Acid number	D 664	0.50 max	0.50 max	mg KOH/g
Free glycerin	D 6584	0.020	0.020	% mass
Total glycerin	D 6584	0.240	0.240	% mass
Phosphorus content	D 4951	0.001 max	0.001 max	% mass
Distillation temperature, atmospheric equivalent temperature, 90% recovered				
	D 1160	360 max	360 max	°C
Sodium and potassium, combined	EN 14538	5 max	5 max	ppm (µg/g)
Oxidation stability	EN 14112	3 min	3 min	hours

Note: For more complete information, refer to the current ASTM D6751 standard.

ADM Biodiesel Typical Properties

COMPOSITION	SOY B100	CANOLA B100
Methyl Esters, % mass	97.5	97.5
Free Glycerin, % mass	0.001	0.001
Total Glycerol, % mass	0.165	0.165
Monoglycerides, % mass	0.575	0.575
Diglycerides, % mass	0.095	0.095
Triglycerides, % mass	0.010	0.010
Methanol Content, % mass	0.110	0.110
Moisture, mg/kg	175	175
Properties		
Density at 15° C	0.8855	0.8831
Viscosity at 40° C, cSt	4.060	4.500
Flash Point, °C	>130	>130
Sulfur Content, % mass	<0.0002	<0.0010
Carbon Residue, % mass	<0.050	<0.050
Sulfated Ash Content, % mass	<0.010	<0.010
Copper Strip Corrosion	1a	1a
Cetane Number	>47	>49
Cloud Point, °F/°C	<36 / <2	<32 / <0
Acid Number, mg KOH/g	0.30	0.15
Phosphorous Content, % mass	<0.001	<0.001
Sodium plus Potassium, ppm	<2	<2
Calcium plus Magnesium, ppm	<1	<1
Oxidation Stability, hours	>8	>8
Cold Filter Plug Point, °C	-4	-13
Distillation Range, °C		
90% recovered	<360	<360
Cold Soak Filtration, seconds	<150	<150
Soap Content, ppm	<10	<10
Color	Straw to Light Amber	Light Straw
Appearance	Clear, Free of Suspended Matter	Clear, Free of Suspended Matter

Specifications

ADM Biodiesel meets and exceeds all of the requirements of the current ASTM D6751, "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillates." ADM Soy Methyl Esters also meet the European specifications of EN 14214, other than the parameters of Cetane Number, Iodine Value and some of the seasonal CFPP requirements. ADM Canola Methyl Esters are fully compliant with both the North American and European standards.

Each of the parameters listed within the specifications is designed, and limits set accordingly, to ensure that the product is fit for purpose. Each result must conform to the specifications to help ensure that biodiesel may be used as a fuel without causing harm. If any parameters are found to not meet these specifications, that fuel is technically not biodiesel and is in jeopardy of losing any applicable tax credits.

Relationship of Properties to Performance

Cold Weather Issues

Cloud Point

While the Cloud Point must be reported, there are no minimum or maximum requirements. It is vital to understand the importance of this value in relation to the performance and handling of B100 at low ambient temperatures. The Cloud Point is the most conservative temperature at which components begin to precipitate from the fuel that may cause operability issues. Cloud Point results will vary significantly depending upon the feedstock from which the methyl ester was created. The following values are general approximations for the corresponding products:

Soy biodiesel	32° F	Tallow biodiesel	50-55° F
Canola biodiesel	27° F	Palm biodiesel	55-60° F

Cold Soak Filtration

The Cold Soak Filtration test is an industry agreed upon parameter as opposed to an ASTM specification. There may be many producers and marketers of biodiesel that do not perform this procedure. However, there is a growing belief that this may be one of the best performance-based predictors of operability. At this time, there are a growing number of customers and U.S. states that require this parameter as a condition of sale. A sample of the fuel is chilled to promote the potential formation of precipitates (one of which may be sterol glucosides). After being allowed to warm to room temperature, the sample is then filtered and timed. Work is ongoing to correlate the filtration time elapsed with a measure of performance in diesel engines.

Monoglycerides

Monoglycerides are partially converted fats and oils found within biodiesel. While not reported separately in the U.S., they are accounted for as part of the total glycerin. The monoglycerides formed as the result of different feedstocks have inherently different properties. They all have somewhat higher melting and Cloud Points, as opposed to the methyl esters. This may lead to the appearance of precipitates just above the reported Cloud Point. It has been shown that the presence of even small amounts of saturated monoglycerides will significantly raise the Cloud Point of biodiesel, while unsaturated monoglycerides will not.[1] These saturated monoglycerides are one of the more common culprits in filter plugging. This material will appear as a thick, waxy coating. The monoglycerides formed from tallow or palm, or those that are saturated by nature, have significantly higher melting points that will require more diligence and more energy to dissolve back into solution. The monoglycerides derived from soy and canola are much less saturated, leading to considerably less impact on filterability.

Corrosion and Deposits

Acid Number

The Acid Number is a relative indicator of the acidic impurities, degradation and/or oxidation of the fuel. Free fatty acids arise in part through the hydrolysis of the feedstock fats and oils. Improper processing or oxidation may also lead to higher values. These oxidative products are associated with fuel system deposits and corrosion. Unfortunately, organic acids vary widely in corrosion properties, and the results cannot be used to predict failures.

Free and Total Glycerin

The Free Glycerin value records the level of by-product glycerin that remains in B100. The Total Glycerin result measures the amounts of unconverted and partially converted fats and oils. Excessive levels of these components may lead to storage tank and fuel system filter plugging, along with engine fouling.

Oxidative Stability

The oxidative stability of the fuel is related in part to the Acid Number results. As the biodiesel degrades, or oxidizes, organic acids or polymers are created as a by-product which may lead to corrosion or filter plugging. The Oxidation Stability result is an accelerated test used to predict the fuel's stability for longer-term storage, possibly up to six months.

Combustion

Cetane Number

Cetane Number for diesel fuel is a rough equivalent to Octane Rating for gasoline. The value provides a measure of the ignition characteristics of the fuel in compression ignition engines. The minimum value allowed for petroleum diesel in North America is 40. The lowest value for typical biodiesel is the same as a "premium petroleum diesel" at 47.

Flash Point

The Flash Point is used in shipping and safety regulations to define flammable and combustible materials. This result is used to determine the classification for the Department of Transportation (DOT) regulations. It is important to note that a typical result of 130° C for biodiesel is almost twice that of petroleum diesel (approximately 70° C) and therefore much safer to handle and transport. The Flash Point is also used to ensure the residual methanol left in the fuel after biodiesel processing will not negatively affect combustion and other fuel system components.

Visual Appearance

While there is no correlation between the color of biodiesel and its performance as a fuel, it is critical that the sample be free of undissolved water, sediment and suspended matter. At room temperature, the sample should be clear and transparent. Any cloudiness or haze may be an indication of impurities or excess water that may be present.

Materials Compatibility

Biodiesel, chemically known as Fatty Acid Methyl Esters (FAME), possesses some solvent-like properties. As such, biodiesel will have a tendency to dissolve the accumulated particulates and sediments found in diesel storage and engine fuel systems. These dissolved sediments may plug fuel filters or injectors, initially. The level of cleaning depends upon the amount of sediment that has accumulated over time and the amount of biodiesel being used.

Methyl esters may also degrade and break down certain elastomers with prolonged exposure. Gaskets, hoses, seals and o-rings are examples of components found in some diesel systems that may experience problems. Plastics, glues and rubber begin to leak and seep as they begin to fail. Older vehicles (manufactured prior to the mid-1990s) are more likely to contain many of the types of materials that would be affected.

Tanks and storage containers may also contain items that could affect the quality and performance of biodiesel. Most tanks are designed to handle fatty acid methyl esters. Acceptable materials include aluminum, steel and most fiberglass. Soft metals, such as brass, bronze, copper, lead, tin or zinc, should be avoided. These compounds are found in many fittings within a fuel system. Their presence will accelerate the oxidation of the fuel, leading to corrosion and the creation of sediments.

The tables below list both recommended and non-recommended elastomer and storage tank materials. The compatibility of individual components should be confirmed with the manufacturer or vendor prior to use.

Recommended for B100

Teflon

Viton

Fluorinated Plastics

Nylon

Aluminum

Carbon, Stainless Steel

Fiberglass (most types)

Not Recommended for B100

Nitrile

Buna N

Natural Rubber

Polypropylene, Polyethylene
(long-term exposure will weaken)

Copper, Brass, Bronze

Lead, Tin, Zinc

Product Handling

Storage

Biodiesel tends to have a slightly greater affinity for water than does petroleum. Because of this, tanks should be checked often for the presence of free water in the bottom of tanks. This water can lead to microbial contamination in the form of bacterial and fungal growth, which may lead to corrosion and filter plugging if not controlled with biocides. Conventional biocides work as well with biodiesel and biodiesel blends as with petroleum diesel fuel. Once the water and microbial contamination is dealt with, cleaning the tank is recommended to ensure that the "dead" organisms do not continue to cause filter plugging.

Seasonally, it may be necessary to warm a vessel of biodiesel prior to the transfer or use of the fuel. B100 freezes at higher temperatures than does petroleum diesel. Insulated and heated fuel lines and tanks are necessary even in moderate climates. It is always better if the temperature of the fuel can be maintained at least 10-15° F above the reported Cloud Point of the product. The Cloud Point of a product is generally accepted to be an index of the lowest temperature that will support operability.

B100 can be a challenge to handle properly throughout the winter. Ensure that any producer is able to maintain the proper product temperature through delivery. Because each feedstock from which the biodiesel is made passes along certain properties, the temperature that each type of methyl ester must be stored at is different. Be sure to ask what the Cloud Point of the B100 is to determine at what temperature the biodiesel must be stored.

If unable to keep the B100 at the necessary temperature, it is advisable to blend the B100 product with petroleum right away. Petroleum diesel fuel has a lower Cloud Point than biodiesel, and therefore allows for handling at lower temperatures prior to the fuel beginning to gel. The addition of biodiesel to petroleum diesel will raise the Cloud Point of the blended fuel slightly relative to the Cloud Point of the original diesel. The greater the percentage of biodiesel added, the more impact that it will have. The ambient temperatures and the expected fuel temperatures should all be monitored to avoid allowing the blends to fall below their respective Cloud Points.

A possible result of B100 that too closely approaches its Cloud Point is that certain components, particularly saturated compounds, begin to crystallize out of solution and settle to the bottom. The amount of heat needed to bring the material back into solution is often times more than the energy required to maintain the original temperature. In bulk storage, the level of the material that has settled over time may become high enough to reach the suction level of the tank. It is at that point that any filters in use, including those on a vehicle, could plug. In extreme cold weather situations, it is also possible for this to occur within a fuel tank and in a filter that is not in use or that has a much lower duty cycle.

Blending

Blending biodiesel with petroleum compensates for many cold flow problems through dilution. As mentioned earlier, the cold flow properties associated with a particular methyl ester are the result of its feedstock. At this time, there are no additives in the marketplace for pure soy methyl esters that can reliably affect these properties as significantly as can be achieved in petroleum diesel. By blending to levels of up to 20% (B20), the use of additives becomes more practical and more effective. The use of #1 diesel, or kerosene, is also an option that many blenders use to help mitigate the effects of cold weather. Testing different mixtures of the actual fuels to be used is the best way to guarantee performance and to determine cost effectiveness. Your local distributor may also have some data or samples of "winterized" fuels.

Biodiesel may also need to be warmed prior to blending. To ensure successful blending into a single mixture, the biodiesel and petroleum should be blended at similar temperatures. Blending products that are at extreme temperature differences will not promote homogeneity within the final blend. The B100 will lend itself to easier mixing with diesel when the biodiesel is at temperatures of at least 25-30° F above the reported Cloud Point.

Product Loading

There are several ways to blend components in order to achieve a homogenous final product. Most often the least effective, but most widely available, is "splash" blending. This is achieved with consecutive loading of products, one loaded on top of another. The blend resulting from this type is dependent upon the agitation of the product and of the vessel to ensure a thorough mix. In colder temperatures, or with widely differing product densities, there are concerns with this type of loading. High load velocity, warm product temperatures and allowing the "heaviest" densities to fill last when loading from the top can help to promote homogeneity. Ratio blending includes sequential loading of the products. The larger-volume product is partially loaded and then stopped to allow the minority product to load. The balance of the larger volume is then completed. Equivalent product temperatures are still important to prevent product separation. "In-line" or "injection" blending requires additional design. Separate load lines are piped together in the shape of a Y prior to reaching the vessel. This design promotes vortex mixing and a uniform product for the duration of the load.

Transportation and Distribution

Trucks

Biodiesel is susceptible to product contamination from both flammable product and water sources. Residual product within a vessel from a prior load poses the largest threat. Because of this, it is recommended that containers and vessels used in the transportation and storage of biodiesel be dedicated in service. If this is not possible, the prior contents of each vessel must be closely scrutinized to avoid product contamination. All vessels presented for load must be completely dry and free of any particulates. Acceptable prior cargoes would only include biodiesel or ultra-low sulfur diesel (ULSD). If the previous contents are not approved, the vessel should be sent for cleaning and a wash certificate.

The vessels themselves must be constructed of approved materials. Biodiesel is compatible with aluminum and stainless steel-constructed trailers. The standard diesel trailer, style MC306, is an oval-shaped tank. While many will be equipped with vapor recovery systems, these are not necessary for methyl esters. Chemical-style trailers, MC307, are round-shaped tanks typically fitted with universal air/nitrogen fittings on top. Compartment trailers vs. single-hole configurations will also play a part in determining how much product can be transported at any given time. Insulated trailers are recommended throughout the winter months to ensure the product integrity. Insulated trailers will typically lose 2-4° F per day, while uninsulated trailers may lose up to 15° F per day of product temperature in cold weather conditions.

Railcars

Most railcars in service are of the DOT 111A or AAR 111A series type. They are constructed of carbon steel and unlined. They have capacities of 25,500 or 29,300 gallons. Low-pressure steam connections are required on the underside to enable the product to be sufficiently heated to completely offload in cold weather.

Attention to prior cargoes and possible contaminants is important. The presence of rust or fine metallic particles accelerates the oxidation process. It is possible to have produced "on-spec" material, only to have it degrade and oxidize to a point that it no longer meets the specifications, which must either be re-processed or disposed of.

Safety, Health & Environmental Issues

Biodiesel contains no hazardous materials and is considered safe to use. In fact, it has been found that methyl esters biodegrade much more rapidly than conventional fuel. Many areas of the country, including our national parks, take advantage of this fact for use in environmentally sensitive regions.

Any additional concerns in respect to safety and health, including first aid and fire fighting measures, may be addressed within the Material Safety Data Sheets (MSDS) relevant to either soy-based or canola-based methyl esters produced by Archer Daniels Midland Company.

Information Resources

Much of the information contained herein and more may be accessed through:

National Biodiesel Board (NBB)
(800) 841-5849
www.biodiesel.org

National Renewable Energy Laboratory (NREL)
www.nrel.gov

American Society for Testing & Materials (ASTM)
www.astm.org

References

1. Yu, L., Lee, I., Hammond, E., Johnson, L., Van Gerpen, J. The Influence of Trace Components on the Melting Point of Methyl Soyate, JAOCS, Vol. 75, no. 12 (1998).

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